AN EXAFS STUDY OF STRONTIUM SORPTION TO HYDROUS MANGANESE OXIDES

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ABSTRACT

Strontium-90 (half-life = 28years),a product of nuclear fission, exists in the environment as a consequence of radioactive waste disposal and other releases associated with the nuclear industry. It is an element ofmajorconcern, froma human health perspective, because of its chemical similarity to calcium and therefore the potential ofits uptake and storage in bones. As a result, the selective retention of strontium byspecific components of soil and natural watersis extremely important because these retardation mechanisms (e.g. adsorption, precipitation, etc.) may prevent migration of the radionuclide for times that assure its decayto insignificance.

Manganese oxides are particularly important solid phases in the environment, where they occur as fine-grained aggregates,crustsand coatings on mineral particles and rocks. Numerous laboratory andfield studieshave revealed the exceptional reactivity of natural manganese phases towards metals.

Inthis study, we conduct macroscopic uptake and molecular-level spectroscopic investigations of thechemical behavior of aqueous Srat the *-Mnoxide solid-solution interface. Sorption isotherms reveal a pronounced affinity of Srfor the Mn oxide surface. The observed uptake behavior is characterized by fast reaction kinetics andsignificant changes in Kd value as a function of strontium concentration. Furthermore, variation in pHand ionic strength had only aminor effect on the uptake behavior.

Synchrotron-based Extended X-rayAbsorption Fine Structure (EXAFS) spectroscopy was used to identify the local coordination environment of the predominant interfacial Sr species. The EXAFS resultsrevealthat manganese occurs in the second coordination shell around Sr at a characteristicSr-Mn distance of approximately 3.6 angstroms over a wide range of solution conditions. This finding is consistent with the formation of inner-sphere Sr sorption complexes on the Mn oxide surface.

Sr-90 IN THE ENVIRONMENT

NUCLIDES IN ACTIVE WASTE - POTENTIAL INGESTION HAZARD

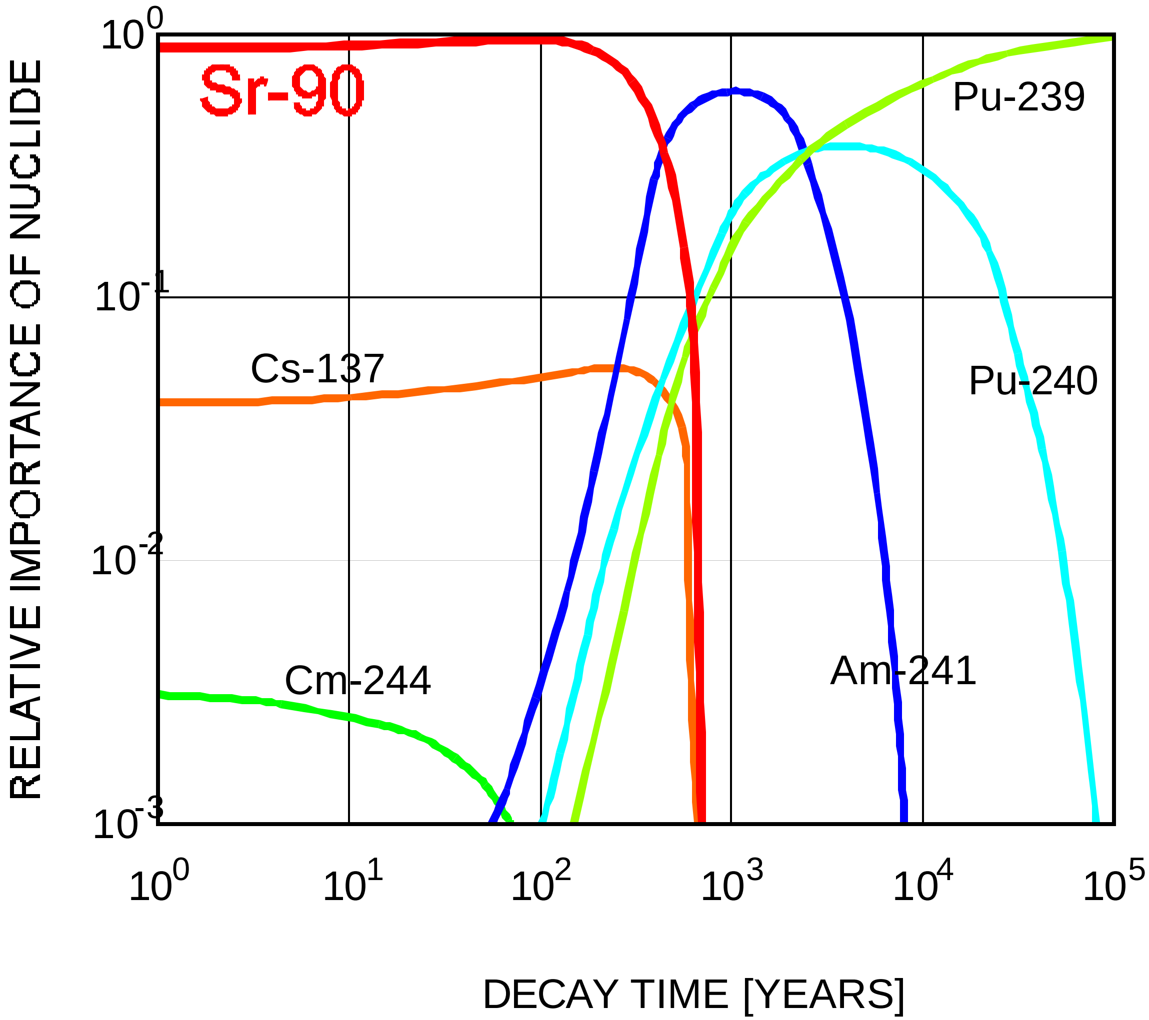
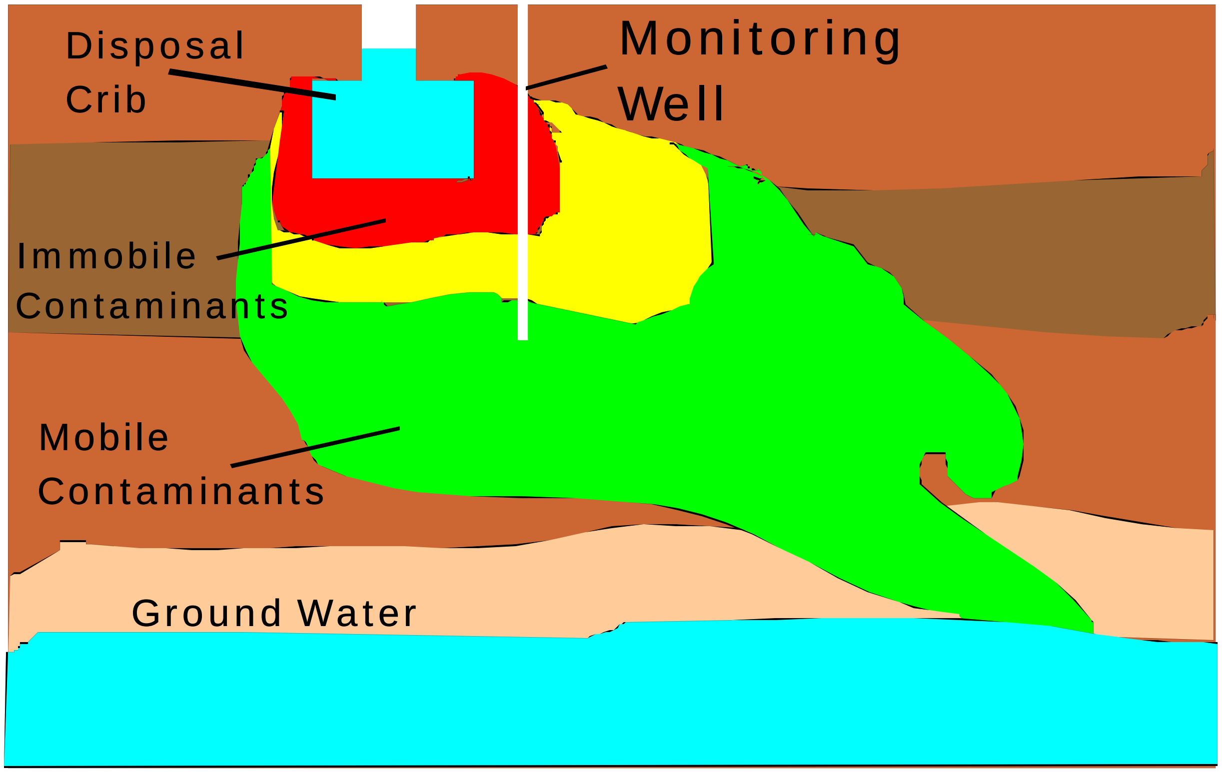


Figure adapted from Martin and Simon, 1988

- Sr-90 is one of the most important radionuclides in the first few hundred years after disposal, based on fission yield, mobility and bioavailability
- Though many lab studies indicate Sr interactions with geomedia are dominated by ion exchange - field studies show significant retardation of Sr

Sr-90 IN THE ENVIRONMENT

- In the past, Sr has been disposed in soil pits and cribs often under alkaline conditions where adsorption to surrounding soil is high
- Natural weathering may mobilize Sr



MATERIALS AND METHODS

- **SUBSTRATE:** δ-MnO_2 (synthetic vernadite)
  - CHARACTERIZATION: BET, x-ray diffraction
  - STRUCTURAL ANALYSIS: Manceau et al., Foster et al., Post et al.

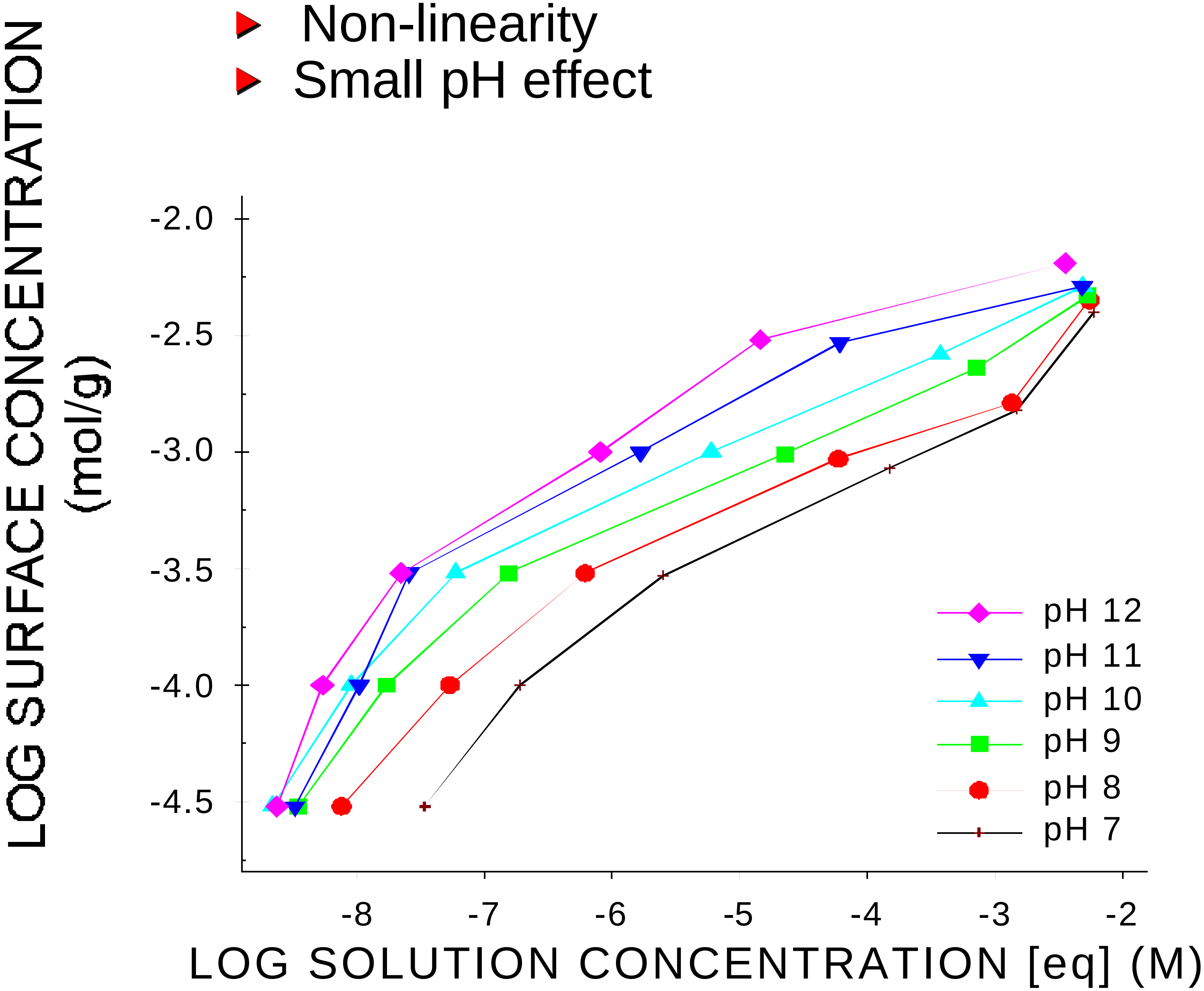
- **MACROSCOPIC UPTAKE STUDIES**
  - BATCH STUDIES: [Sr], Equilibration Time, Ionic Strength (IS), pH, pCO_2

- **SPECTROSCOPIC STUDIES**
  - EXAFS: Model compounds and Sorption Samples
  - DATA COLLECTION: SSRL BL 4-3 [3GeV,~80mA], Si(111) / Si (220)
Transmission (Ion chambers) / Fluorescence (Canberra Ge13)
Room-Temp. and Cyro-Temp. (~25K), multiple scans
  - DATA ANALYSIS: EXAFSPAK[1], XAFS[2], WinXAS[3]

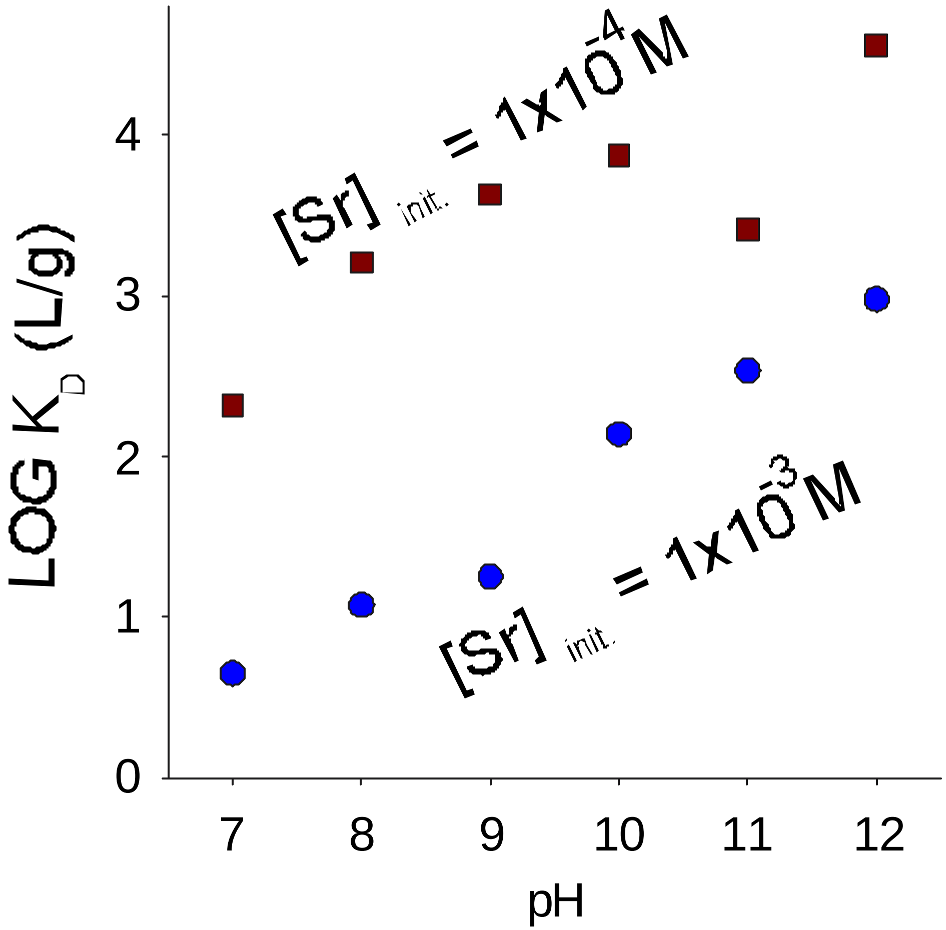
[1] and Pickering (1990), [2]Winterer (1996),[3]Ressler (1997)

MACROSCOPIC SORPTION OF Sr(II) ON δ-MnO_2

- Non-linearity
- Small pH effect



MACROSCOPIC SORPTION OF Sr(II) ON δ-MnO_2

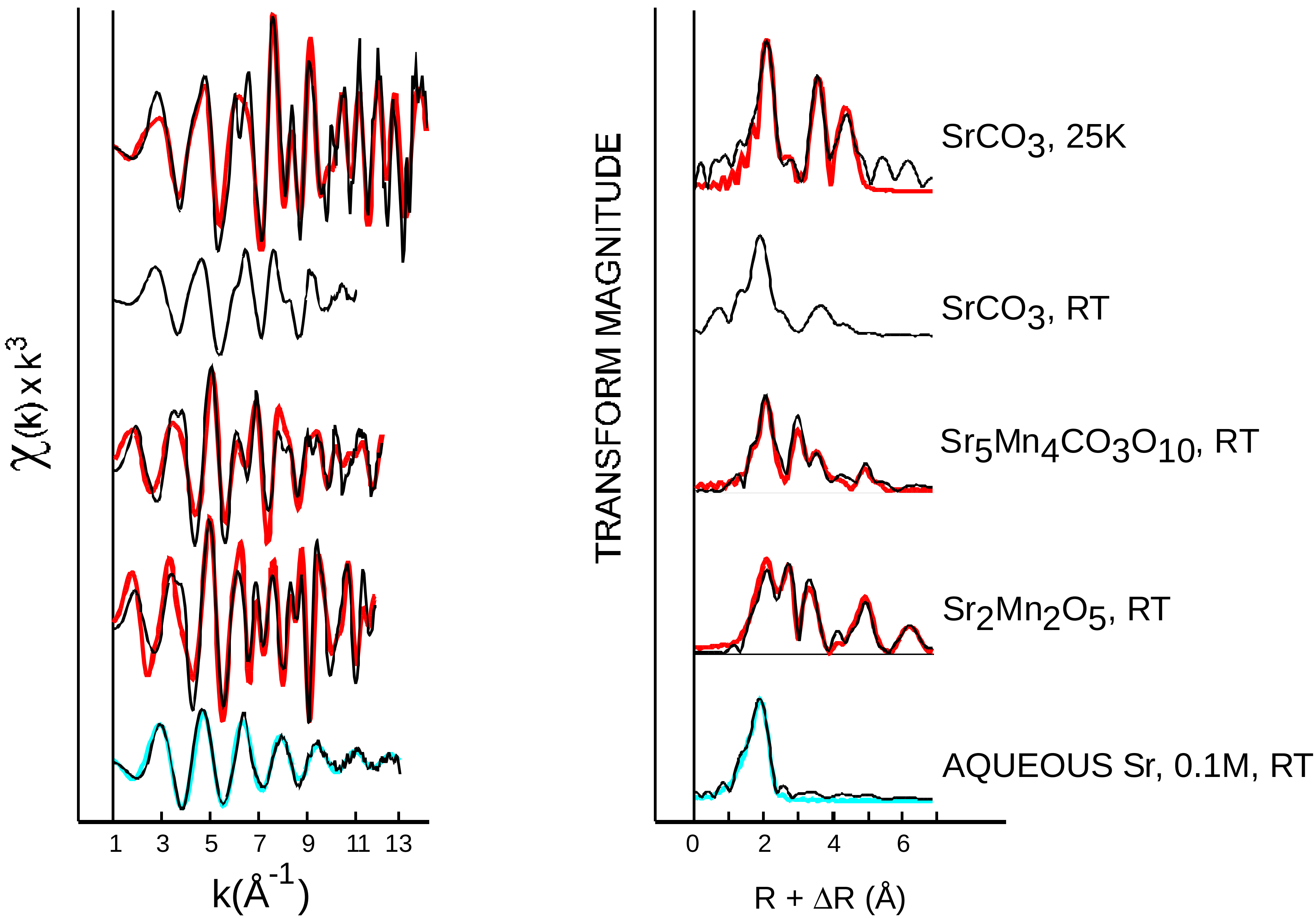


Percentage of Sr strongly* bound to MnO_2

[Sr] initial (M)	pH 7	pH 9	pH 11
0.001 M	0.5	2.3	4.5
0.0001 M	1.9	2.5	4.1

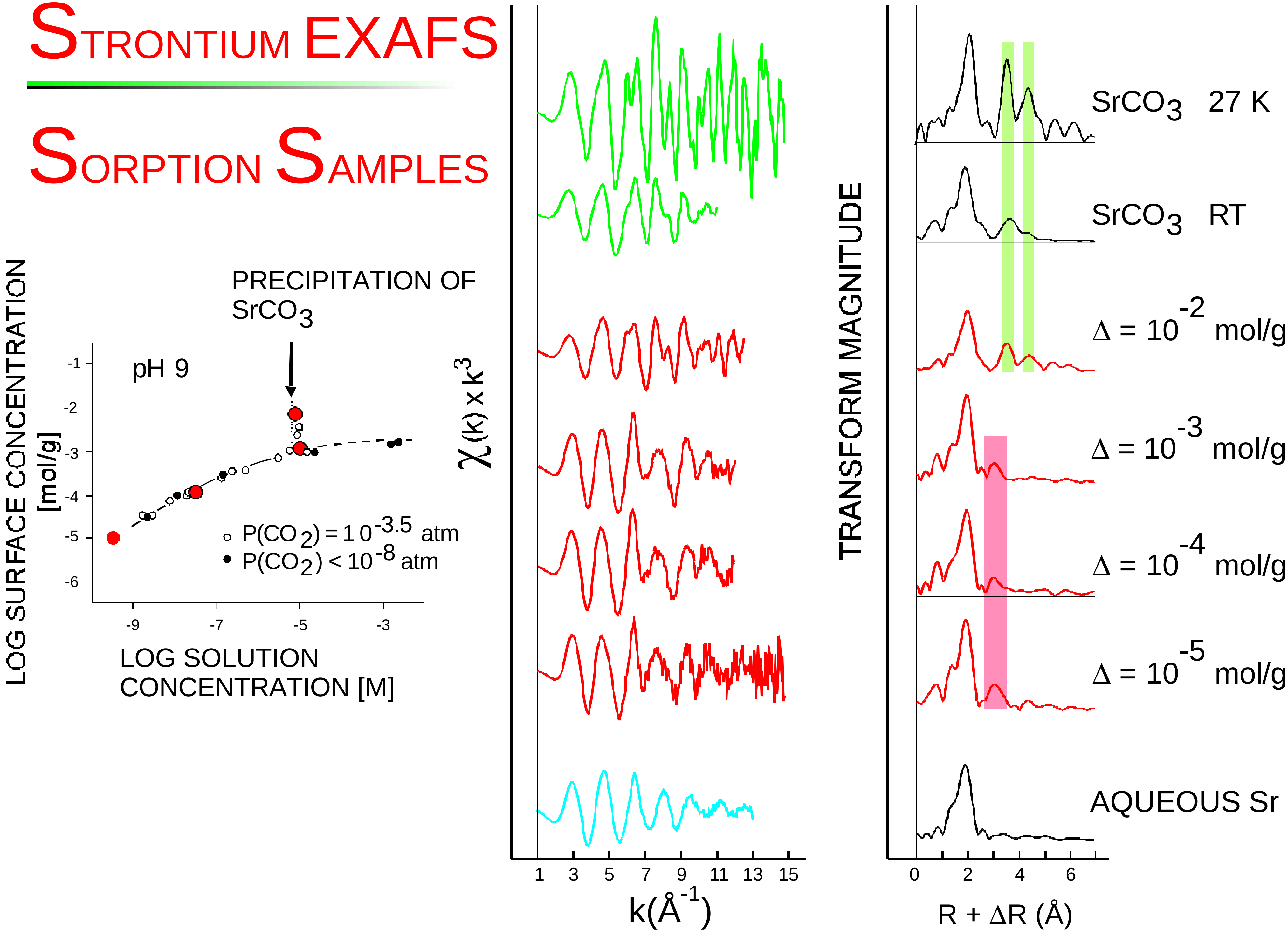
* as determined from microwave assisted acid digestion after desorption with acidified 1 M $NaNO_3$

Sr K-edge EXAFS - Model Compounds



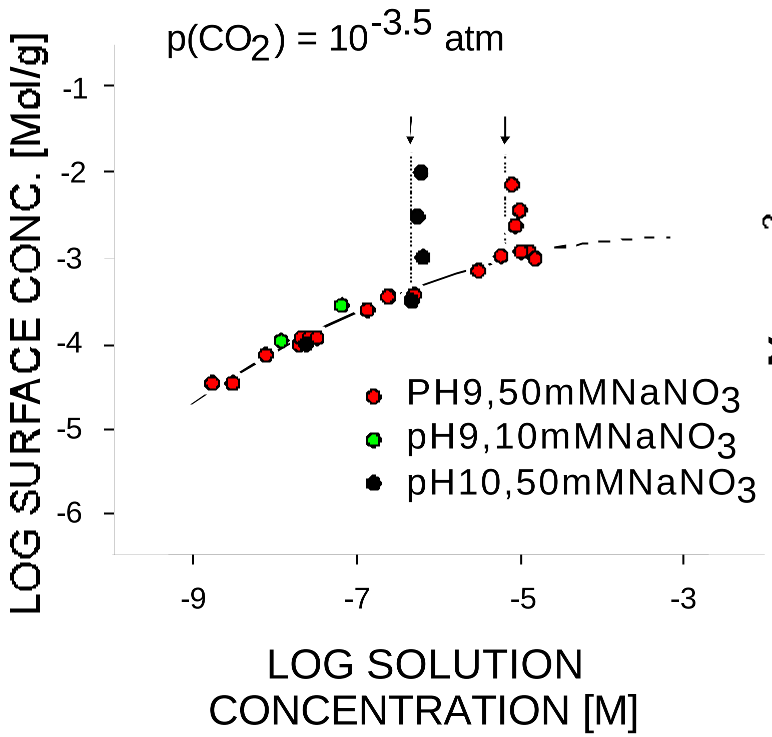
STRONTIUM EXAFS

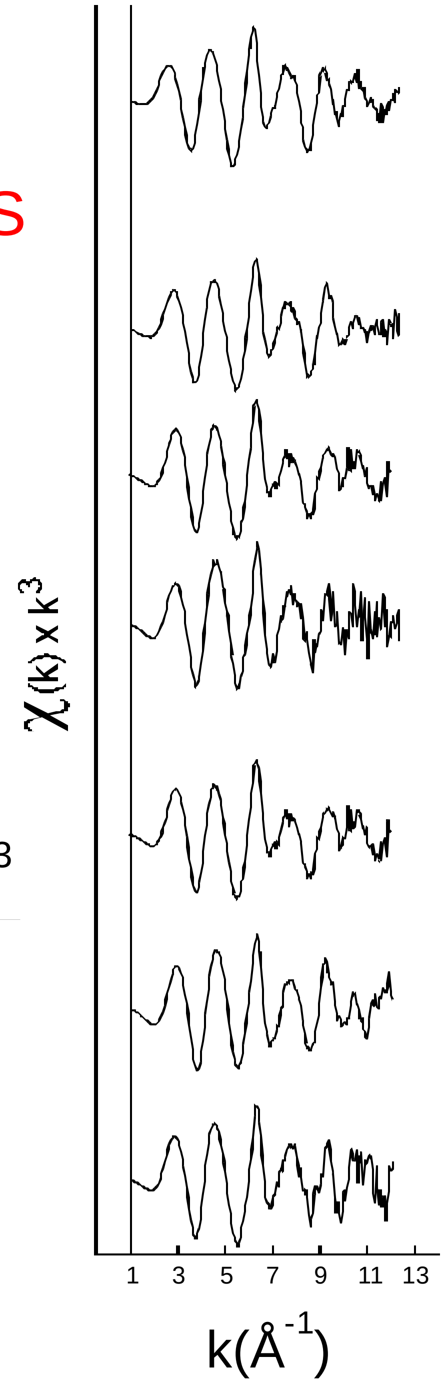
SORPTION SAMPLES

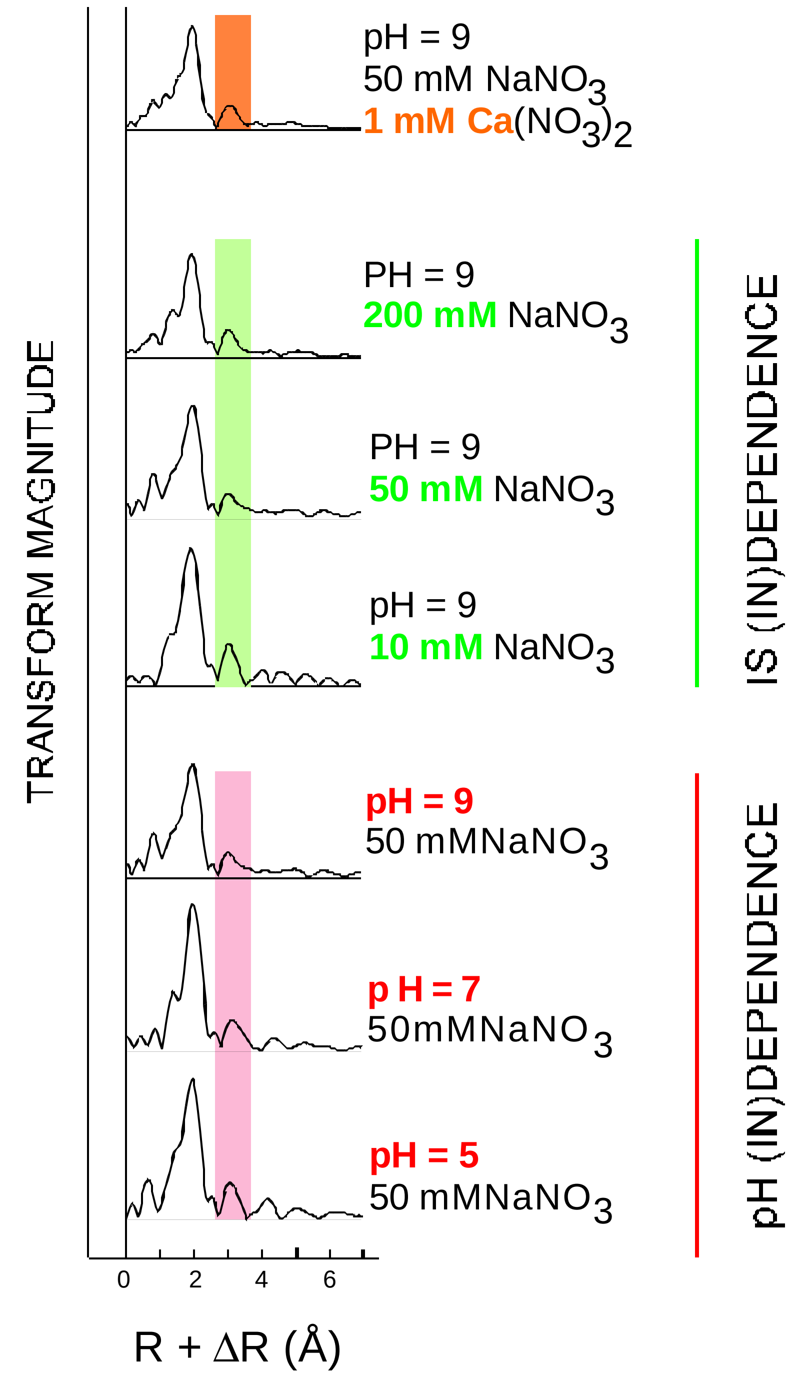


Strontium EXAFS

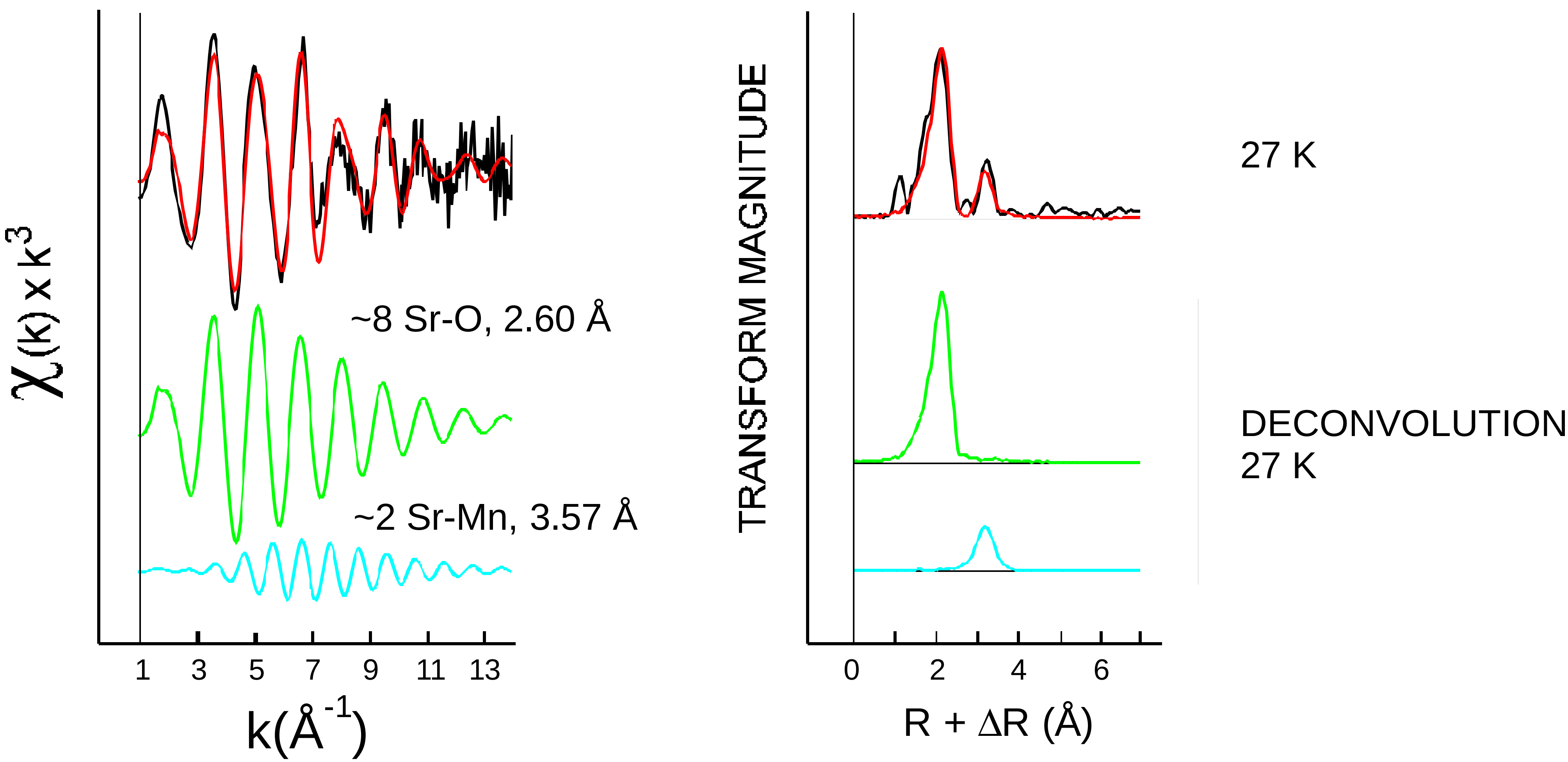
Sorption Samples







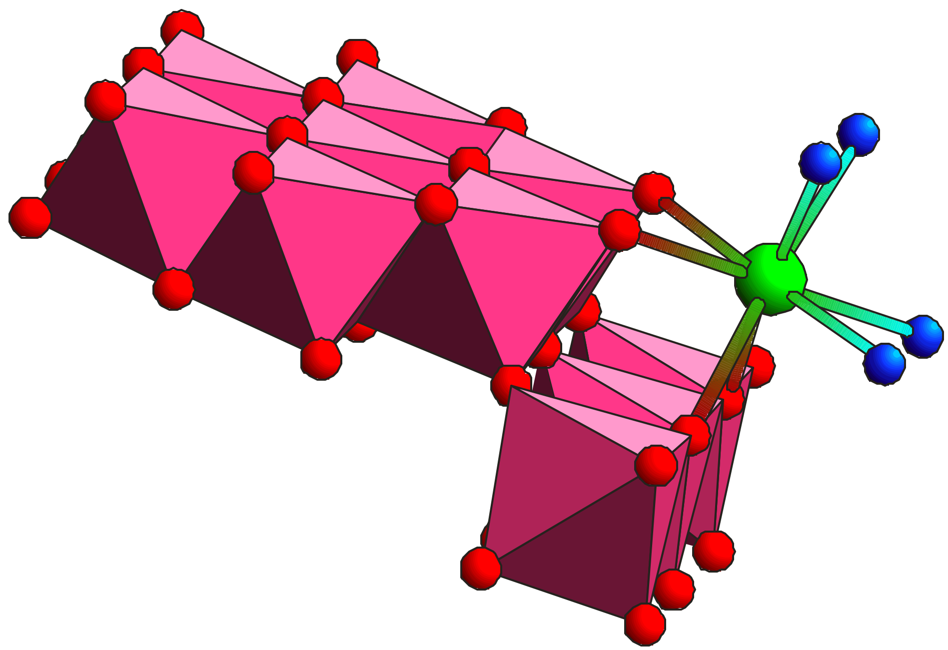
Strontium - Model Compounds



PROPOSED INTERFACIAL COMPLEX

'INNER-SPHERE'
COVALENT BONDING

STRONTIUM
SURFACE HYDROXYL



SUMMARY • CONCLUSIONS

- BASED ON FISSION YIELD, HALF-LIFE, BIOLOGICAL ACTIVITYANDMOBILITY Sr-90 ISONE OF THE MOST IMPORTANT RADIONUCLIDES, IN TERMS OF HUMAN HEALTH, IN THE FIRST FEW HUNDRED YEARS AFTER DISPOSAL.

- MACROSCOPIC UPTAKEISOTHERMS OF Sr ON HYDROUS MANGANESE OXIDES (*-MnO_2) INDICATE INCREASING SORPTION WITH INCREASING STRONTIUM INITIAL CONCENTRATIONANDINCREASING pH.

- EXAFS SPECTROSCOPY SHOWS A SECOND SHELL FEATURE AT A 3.6ANGSTROMS, OVER A WIDERANGE OF SOLUTION CONDITIONS, WHICH IS ATTRIBUTED TO Sr - Mn. THIS FINDING IS CONSISTENT WITH THE FORMATION OF INNER-SPHERE S r SORPTION COMPLEXES ON THE Mn OXIDE SURFACE.
  - THIS INTERPRETATIONIS ALSO S UPPORTED BY DESORPTIONDATA S HOWING STRONGLY BOUND Sr A FTER TOTAL DIGESTION OF T HE REACTED SOLID.

- THAT A SIGNIFICANT FRACTION OF Sr IS INNER-SPHERICALLY BOUND TO THE *-MnO_2 SURFACE HAS IMPORTANT IMPLICATIONS FOR THE TRANSPORTAND FATE OF Sr IN THE ENVIRONMENT.

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